

## Heptamethyltrisilane-2-thiol-mediated Free-radical-chain Reduction of Organic Halides†

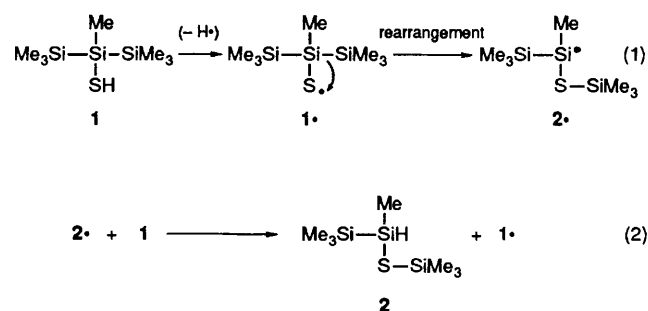
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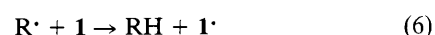
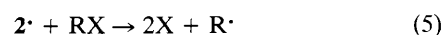
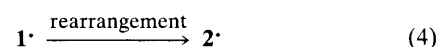
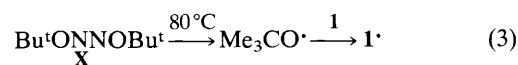
Free-radical-chain reduction of organic halides is accomplished with heptamethyltrisilanethiol, a reducing agent combining the good hydrogen donating ability of a thiol and the excellent halogen abstracting properties of a silyl radical.

Trialkyltin hydrides are the most commonly employed reagents for reducing alkyl halides by a free-radical-chain reaction.<sup>1</sup> However, tin hydrides suffer from the disadvantage that it is often difficult to separate the tin residues from the desired product and from the fact that organotin compounds are toxic. To overcome these problems, several alternative radical chain reducing agents for organic halides have been proposed,<sup>2-6</sup> most of which are based on silicon hydrides.<sup>3-6</sup> Silyl radicals are more effective halogen atom abstracting agents than tin radicals<sup>7</sup> but the Si-H bond in trialkylsilanes is not cleaved by alkyl radicals and this precludes the direct use of trialkylsilanes as reducing agents for alkyl halides. This difficulty has been overcome by the use of various silicon substituted silanes<sup>3,4</sup> and by a catalytic combination of a trialkylsilane and alkyl thiols.<sup>5</sup> Thiols are, of course, very good hydrogen donors to alkyl radicals<sup>8,9</sup> and can be used as reducing agents in Barton-type chain reactions.<sup>8,10</sup> However, by themselves thiols will not reduce alkyl halides because thiyl radicals do not abstract halogen atoms.



A report by Pitt and Fowler<sup>11</sup> on the free radical transformation of heptamethyltrisilane-2-thiol into the corresponding sulphide, reactions (1) and (2), prompted us to test **1** as a reducing agent. Our novel idea was to make use of the  $\mathbf{1}\cdot \rightarrow \mathbf{2}\cdot$  rearrangement so that the hydrogen donating ability of a thiol **1** would be combined with the halogen abstracting ability of a silyl radical  $\mathbf{2}\cdot$ .

Compound **1** was synthesized following a literature procedure<sup>11,12</sup> and was identified *via* its <sup>1</sup>H NMR and mass spectra. To our disappointment, **1** was less stable than originally reported<sup>12</sup> and our attempts to obtain it as a pure material by distillation (even in the presence of the free radical inhibitor, hydroquinone) resulted in the formation of substantial amounts of **2**. Our experiments on halide reduction were, therefore, carried out with benzene solutions<sup>‡</sup> of **1** which were shown by VPC to contain only the desired thiol. The radical chain reductions of some organo halides, RX, at 80 °C, were initiated by the thermal decomposition of di-*tert*-butyl hypodinitrite **X**, reactions (3)–(6). Product yields are given in Table 1.



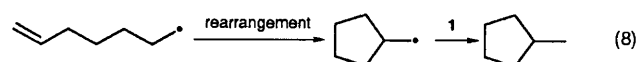
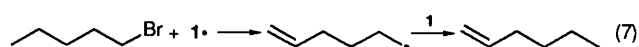
† NRCC publication No. 32822.

‡ Compound **1** appears to be more stable in benzene than in alkane solutions.

**Table 1** Hydrocarbon yields for the reduction of halides RX by **1** at 80 °C in benzene<sup>a</sup>

R	X	Yield (%)
Bu <sup>n</sup>	Br	95
Octan-1-yl	Br	98
Decan-1-yl	Br	96
Octan-2-yl	Br	92
1-Adamantyl	Br	100
Octan-1-yl	Cl	75
Octan-2-yl	Cl	88
1-Adamantyl	Cl	94
Ph	Br	24
Ph	I	97

<sup>a</sup> Reactions were carried out for 1 h at 80 °C with *ca.* 0.15 mol dm<sup>-3</sup> RX and *ca.* 0.3 mol dm<sup>-3</sup> **1** in the presence of *ca.* 3 mol% of an initiator. Yields are by VPC analysis based on the formation of RH.



The reductions of alkyl bromides and iodobenzene were (within experimental error) quantitative. Although the yields of hydrocarbons in alkyl chloride reductions§ were not 100%, they were still gratifyingly high.¶ Residual chlorides were present in these reaction mixtures, together with some **2**,|| which is the product of the competing reaction (2). Bromobenzene was reduced in 24% yield while substantial quantities of **2** were also produced.

§ The decrease in hydrocarbon yields along the series 1-adamantyl, octan-2-yl, and octan-1-yl chloride probably reflects the diminishing competitiveness of reaction (5) *vs.* reaction (2).

¶ Particularly so since the reactions were carried out in benzene to which silyl radicals add readily.<sup>13</sup> Our results thus confirm earlier reports<sup>14</sup> that silyl radical addition to aromatics must be reversible.

|| Not unexpectedly, in view of the recent findings on reducing properties of the tri(alkylthio)silane,<sup>6</sup> **2** also proved to be a rather effective reducing agent. Thus, it converted alkyl bromides quantitatively into the corresponding hydrocarbons in a free-radical-chain process. This raises the possibility that **2** is at least partially responsible for the reductions in our system in cases where reaction (2) successfully competes with reaction (5), *i.e.* in alkyl chloride reductions.

Application of the hex-5-enyl 'clock'<sup>15,16</sup> reactions (7) and (8) gave a rate constant of *ca.*  $3 \times 10^7$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> for hydrogen abstraction from **1** at 80 °C by a primary carbon-centred radical.\*\*

In conclusion, the polysilyl thiol **1** combines good hydrogen atom donation with, after rearrangement, excellent halogen atom abstracting ability. This compound demonstrates a new concept for the radical chain reduction of alkyl halides, which we believe can be developed and improved.

We gratefully acknowledge a NATO travel grant (J. L., C. N., B. M.) and an NRCC President's grant (J. L., J. D.).

Received, 8th January 1991; Com. 1/00098E

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\*\* The rate constant for hydrogen abstraction from *tert*-butyl thiol at 80 °C is  $1.35 \times 10^7$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.<sup>8</sup>